

RESERVE COPY.

PATENT SPECIFICATION

NO DRAWINGS

851753



Date of Application and filing Complete Specification: Nov. 13, 1957.

No. 35420/57.

Two Applications made in United States of America on Nov. 23, 1956.

Complete Specification Published: Oct. 19, 1960.

Index at acceptance:—Class 2(6), P10A, P10C(2:3:7:8B:12B:12X:13A:14B:18:20D1:20D3), P10D(1A:1X:2A), P10K(4:5:6:8:10), P10S3.

International Classification:—C08f.

COMPLETE SPECIFICATION

Vinyl Chloride Resin Compositions

We, UNION CARBIDE CORPORATION, a Corporation organised and existing under the Laws of the State of New York, United States of America, of 30, East 42nd Street, New York 17, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to resinous mixtures and more particularly to mixtures comprising resinous homopolymers or copolymers or both of vinyl chloride and esters of isophthalic acid or terephthalic acid or both.

It is known that articles formed from vinyl chloride resin mixtures or compositions which contain plasticizers, such as dioctyl phthalate or tricresyl phosphate, when left in contact with surfaces coated with nitrocellulose lacquer, or articles formed from or coated with cellulose butyrate-acetate, the plasticizer tends to migrate from the vinyl chloride resin composition into the surface of the material with which it is in contact. As a result of this migration, the material receiving the plasticizer usually suffers a decrease in surface hardness smoothness and gloss. A material whose appearance has thus been affected in this manner is said to have been "marred;" and the process that brings about these effects is termed "marring."

The marring tendency of a vinyl chloride resinous composition or mixture is conveniently measured by noting the decrease in hardness of the material with which it has been in contact.

"Retractability," as used herein, denotes a property of a viscoelastic body to resume its former shape when a distorting force is removed. Retractability is an especially desirable property in such objects as electrical cords for telephone hand sets and foam cushions. Retractability is commonly imparted to vinyl chloride resinous compositions by incorporating therein low molecular weight plasticizers and it increases with an increase in the content of low molecular weight plasticizer.

This increased retractability is, however, accompanied by an increase in the marring effect on such surfaces as nitrocellulose lacquers which may be in contact with the article. Consequently the amount of low molecular weight plasticizers used in vinyl chloride resinous mixtures is somewhat controlled by the degree of retractability desired, on one hand, and the deleterious marring effect, on the other hand.

In order to minimize marring, vinyl chloride resinous compositions have been plasticized with high molecular weight plasticizers. Illustrative of such high molecular weight plasticizers are polyesters obtained from dibasic organic acids and glycols and epoxidized soy bean oils. The marring produced by these high molecular weight plasticizers is generally less than that produced by low molecular weight plasticizers. However, high molecular weight plasticizers have been found to impart other undesirable qualities to vinyl chloride resins to a greater degree than low molecular weight plasticizers.

We have found that articles formed or coated with vinyl chloride resins in admixture with 15 parts to 100 parts of esters of isophthalic and terephthalic acids and having structures represented by the graphical formula (1) described hereafter, per 100 parts by weight of vinyl chloride resin, do not mar to any appreciable extent and are superior, as far as non-marring properties are concerned, to vinyl-chloride resin admixtures containing known low molecular weight plasticizers.

The plasticizers used in the vinyl chloride resinous mixtures of this invention may be represented by the graphical formula:



wherein: Y is a meta-phenylene or a para-phenylene group; R^1 is an alkyl group containing from 4 to 12 carbon atoms; R^{11} is an alkyl group containing from 4 to 12 carbon atoms, or a phenyl group, or an alkaryl group, or an aralkyl group; and R^1 and R^{11} may be the same or different groups. The preferred

esters have the graphical formula (1) wherein: Y is the meta-phenylene group and R¹ and R¹¹ are the same or different alkyl groups, each of which contains from 6 to 10 carbon atoms.

5 Illustrative of the plasticizers useful in our mixtures are the dioctyl isophthalates such as di-2-ethylhexyl isophthalate, the didecyl isophthalates such as the isophthalates derived from isophthalic acid and the mixtures of
10 decyl alcohols, butyl decyl isophthalate, butyl benzyl terephthalate or octyl tolyl isophthalate.

According to the present invention a resinous mixture having improved non-marring characteristics, comprises a vinyl chloride resin containing at least 85% by weight of polymerized vinyl chloride, and an organic ester having the formula: R¹OOC—Y—COOR¹¹ in which
15 Y is a meta- or para-phenylene radical, R¹ is an alkyl radical containing 4 to 12 carbon atoms, and R¹¹ is an alkyl radical containing 4 to 12 carbon atoms or a phenyl, aralkyl or an alkaryl.

The compatibility of some of the esters represented by graphical formula (1) with vinyl chloride resins affects the amount of ester that can be used efficiently. By way of illustration, no more than 40 parts by weight of didecyl isophthalate are compatible with 100 parts by
25 weight of a vinyl chloride resin. However, we have found that when from 40 parts to 60 parts and 40 to 100 parts by weight of this ester per 100 parts by weight of resin were used in the cold and hot processed admixtures respectively of the present invention, no significant marring of a nitrocellulose lacquer occurred even though some of the ester was
35 exuded from the mixture and came directly into contact with the surface of the nitrocellulose lacquer.

As used herein the term "vinyl chloride resins" signifies both resinous homopolymers of vinyl chloride and also resinous copolymers of vinyl chloride and another vinyl or a vinylidene compound. The vinyl chloride resins that are useful in our admixtures contain at least 85% by weight of vinyl chloride and up to 15% by weight of another copolymerized vinyl or vinylidene compound. Illustrative of the
40 types of vinyl or vinylidene compounds that can be copolymerized with vinyl chloride are vinyl esters, vinyl ethers, vinyl ketones, vinyl and vinylidene halides, acrylic compounds and allylic compounds. Specific examples of these
45 vinyl and vinylidene compounds are vinyl acetate, methyl acrylate vinyl ethyl ether, allylidene diacetate, vinyl methyl ketone, vinyl bromide, or vinylidene chloride.

Esters represented by graphical formula (1) can be used either individually or in various combinations with one another as plasticizers in the admixtures. When a mixture of plasticizers is used with a vinyl chloride resin each plasticizer contributes proportionately to the
50 marring produced to the same extent as it

would were it the sole plasticizer. Hence, when mixtures of these esters are used as plasticizers no significant marring is caused by the resulting admixture because the individual esters when
55 used alone as plasticizers in the same amounts do not cause significant marring. In similar manner, the degree of marring induced by a mixture of plasticizer consisting of a non-marring isophthalate or terephthalate ester and a conventional, marring plasticizer is less than that induced by an equal amount of the marring plasticizer used alone. Known plasticizers, such as trioctyl phosphate, can be incorporated with the mixtures of this invention to provide some particular balance of properties in the coating or in the articles formed therefrom.

The admixtures of the present invention may comprise other components in addition to those hereinbefore disclosed. The additional components can be any of the stabilizers such as dibasic lead phosphite or dibasic lead stearate; colorants; fillers; extenders; densifying agents; opacifying agents; and other modifiers such as are commonly used in connection with known vinyl chloride resins.

The plasticized compositions of this invention include plastisols and hot-processed compounds.

As used in this specification the term "plastisol" denotes a mixture of a resin and the plasticizer that is formed at about room temperature. The plastisols of this invention are formed by mixing an ester that may be represented by the graphical formula (1) and the vinyl chloride resin along with, or without, the above-mentioned components at about room temperature. The vinyl chloride resins used in the preparation of the plastisols are in the form of finely divided particles having diameters preferably in the range from 0.05 to 2 microns. Vinyl chloride resins of the above-mentioned particle size may be produced by aqueous emulsion polymerization techniques such as described in U.S. Patent No. 2,068,424.

Apparatus which is customarily used for preparing plastisols, e.g. a Hobart blender, is suitable for mixing the plastisol compositions of the present invention.

The plastisols of the present invention may be moulded by any of the known techniques. Thus, they can be moulded in a closed, heated mould, or slush moulded, or cast from solution; or the plastisols may be mixed with liquid organic compounds to form organosols which may then be processed by known methods.

The plastisols may be formed into foam cushions in which they exhibit good retractability (elastic recovery), and "non-marring" properties when placed in contact with, e.g. nitrocellulose lacquers on furniture; they are also particularly suitable for the manufacture of other articles that come into contact with

surfaces such as nitrocellulose lacquered table tops.

In producing the hot-processed compositions of our invention the process employed to form a mixture of the ester that may be represented by the graphical formula (1) and the vinyl chloride resin along with, or without, other components was found to be critical in imparting essentially "non-marring" properties to our compositions especially when larger amounts of the esters were used. The process for forming such mixtures includes mechanically mixing the components of our composition at a shearing pressure and temperature high enough to flux the resin.

The temperature should be less than that at which excessive thermal degradation occurs. Some or all of the heat required is imparted to the components via the conversion of some of the mixing energy into heat due to friction in the mixing zone. External heat may be supplied, if necessary, by the use of heating coils in or around the mixing apparatus, or excessive heat may be removed by cooling water to prevent undue thermal degradation of the resin. The hot mixing of the components of the admixture can be accomplished in a mixer, on a two roll mill, in a mixing extruder or by means of other equipment used to mix and flux thermoplastic resins. Prior to the above-described mixing operations a preblend may be prepared by mixing the components in ribbon or paddle type blenders, conical blenders, tumbling drums or other mixing equipment. The various components may all be mixed together or may be combined in any sequence to promote better uniformity of all overall composition.

The hot processed mixture can be extruded, calendered or moulded by any of the methods commonly used to form wire insulation, sheets or any of the plastic products commonly produced from known vinyl chloride resins.

In some instances the hot processing and

forming operations may be accomplished advantageously in the same piece of equipment. For instance, a pre-blend can be charged directly into an extruder and the pre-blended mixture can be hot mixed and fluxed in the barrel portion of the extruder and formed, for example, into wire insulation, by passage through the die portion of the extruder.

In the following examples illustrating the present invention, marring was measured as follows: Press-polished 0.020" thick test specimens were kept in contact with a nitrocellulose lacquered glass plate under a pressure of one pound/sq. in. for 24 hours at 40° C. The plate was then cooled to 23° C. and maintained at this temperature for two hours. The softening of the lacquer film was then measured. A Walker-Steele Swinging Beam Hardness Tester was used to measure initial and final lacquer film hardness. Marring was reported as "per cent. softening," i.e., per cent. hardness decrease. Values of marring of 10% or less as obtained by the above-described test are of questionable significance and so values of marring of 10% or less should be regarded as indicating no marring.

The nitrocellulose lacquer that was used in the marring tests was applied to 6 inch x 6 inch glass plates using a bladed instrument that was set to provide a 3 mil clearance and was 2 inches wide. The lacquer was dried on the glass plates overnight at room temperature. It was then dried for 2 hours at 60° C. and finally cooled to room temperature, at which temperature it was maintained for at least 2 hours. The coatings so formed were about 2 inches wide and from 0.8 to 1.0 mil thick. The plates so treated were stored at about 23° C. and 50% relative humidity until needed for the tests.

All parts and percentages used herein are parts and percentages by weight unless otherwise stated.

EXAMPLE I

Five admixtures (A, B, C, D and E) consisting of:

copolymer containing about 95%
vinyl chloride and about 5%
vinyl acetate

100 Parts

dibasic lead phosphite

2 parts

dibasic lead stearate
plasticizer

1 part
as shown below

were hot processed in the following manner. The materials indicated were thoroughly pre-blended, then fluxed and sheeted on a two roll mill at 170° C. The roll sheet was then given 10 end-passes through the rolls. Samples of 20, 40 and 80 mil thickness, the thickness of

each sample having been obtained by appropriately changing the roll opening, were removed from the roll mill. The remaining material was calendered into 4 mil film. This film and appropriate test specimens moulded from the 20, 40 and 80 mil roll sheet samples

were then tested for the various properties shown below:

The alcohols used in producing the "didecyl" esters tested in this and the other examples

were a mixture of decanols produced by reacting carbon monoxide, an olefin, and hydrogen in the presence of a catalyst such as iron carbonyl.

5

Plasticizer: (parts by weight)	A	B	C	D	E
di-2-ethylhexyl phthalate	50	—	—	—	—
didecyl phthalate	—	50	—	—	—
di-2-ethylhexyl isophthalate	—	—	50	—	—
mixture of 85 parts di-2-ethylhexyl isophthalate and 15 parts di-2-ethylhexyl terephthalate	—	—	—	50	70
Test Results:					
Hardness, Durometer "A"	77	84	80	80	63
Tensile Strength, (Pounds/Sq. in.)	3390	3230	3270	3180	2590
Ultimate Elongation (%)	291	275	314	260	300
Stiffness at 23°C. (Pounds/Sq. in.)	1100	1920	1450	1600	780
Brittle Temperature (°C.)	-22	-24	-24	-26	-36
Plasticizer Permanence:					
SPI Volatility (%)	3.9	1.3	2.2	2.7	3.1
Water Extraction (%)	1.2	0.4	1.5	0.6	0.6
Oil Extraction (Constant)	1.5	1.3	1.8	1.3	5.1
Marring (%)	45	42	<10	<10	13

- 10 Admixtures C, D and E are typical of compositions that are used in producing sheeting for drapes.

EXAMPLE II.

Two admixtures (A and B) having the com-

ponents shown below were hot processed as in Example I. The 4 mil films and the moulded pieces obtained thereby were tested with the following results:

15

Admixtures:	A	B
copolymer containing about 95 parts vinyl chloride and 5 parts vinyl acetate	100	100
tri-2-ethylhexyl phosphate	28.6	28.6
di-2-ethylhexyl phthalate	26.4	—
di-2-ethylhexyl isophthalate	—	26.4
hexyl epoxy stearate (commercial grade)	5.0	5.0
60-40 parts barium-cadmium laurate	2.0	2.0
triphenyl phosphite	1.0	1.0
Test Results:		
Specific gravity	1.199	1.198
Durometer "A" hardness	68	70
SPI Volatility (%)	8.4	6.5
Brittle Temperature (°C.)	-50	-50
T ₄ (°C.)	-11	-15
Water Extraction (%)	2.2	1.1
Marring (%)	>90	55

- 20 Admixture B is typical of materials that are used in producing upholstery sheeting. "T₄" represents the temperature at which the admixture has a stiffness of 10⁴ pounds per square inch.

EXAMPLE III.

Four admixtures (A, B, C and D) were prepared by a hot process as in Example I and tested. The admixtures prepared had the following components:

25

Component	Parts			
copolymer containing about 95 parts vinyl chloride and 5 parts vinyl acetate	100			
dibasic lead phosphite	2			
dibasic lead stearate	1			
plasticizer (types and proportions shown below)	50			
Plasticizer	A	B	C	D
di-2-ethylhexyl isophthalate	50	—	42.5	42.5
di-2-ethylhexyl phthalate	—	50	7.5	—
di-2-ethylhexyl terephthalate	—	—	—	7.5
	Marring (%)			
	A	B	C	D
	4.6	50	10	7.4

Admixtures A and D are typical of those used in producing calendered films and sheets.

EXAMPLE IV.

5 Four admixtures (A, B, C and D) were prepared and tested. The admixtures contained

50 parts of the indicated plasticizer per 100 parts of the resin (which resin was a copolymer containing about 95 parts by weight vinyl chloride and 5 parts by weight vinyl acetate). 10
The admixtures were prepared by the hot process method described in Example I.

Admixture	Plasticizer	Marring (%)
A	di-2-ethylhexyl phthalate	50
B	a mixture of 15 parts di-2-ethylhexyl phthalate and 85 parts di-2-ethylhexyl isophthalate	10
C	di-2-ethylhexyl isophthalate (average of 4 runs)	less than 10
D	a mixture of 50 parts didecyl isophthalate and 50 parts di-2-ethylhexyl isophthalate	less than 10

15 Admixtures C and D are typical of those used in producing sheeting for drapes.

EXAMPLE V.

Two admixtures (A and B) were prepared

by a hot process method similar to that used in Example I and they had the following components: 20

copolymer containing about 95 parts vinyl chloride and 5 parts vinyl acetate	100	100
polyester plasticizer*	50	—
di-2-ethylhexyl isophthalate	—	50
dibasic lead phosphite	2	2
dibasic lead stearate	1	1

25 *This plasticizer was a liquid that had the following physical properties at 20° C.: Specific Gravity of 1.084, viscosity of 3000 centipoises and refractive index of 1.470. This plasticizer is typical of the high molecular

weight plasticizers used in known vinyl chloride resin compositions.

Admixtures A and B were found to have the following properties: 30

	A	B
Hardness, Durometer "A"	88	78
Stiffness at 23°C. (psi)	4100	1650
Brittle Temperature (°C.)	-6	-24
Marring (%)	18	less than 10

Admixture B is typical of those used in producing extruded gaskets.

EXAMPLE VI.

- 5 An admixture having the following components based on 100 parts by weight of the admixture was prepared: 52.8 parts of a copolymer containing 95 parts vinyl chloride and 5 parts vinyl acetate, 2 parts barium laurate, 10 0.2 parts high melting refined paraffin wax, 3 parts epoxidized soy bean oil and 42 parts dioctyl isophthalate.

- The components were mixed by a hot process in a mixer for 8 minutes under a ram pressure of 20 psi. Steam was applied to the jacket and the rotors of the mixer during the mixing at such a rate that the temperature of the mass rose gradually from 155° C. to 160° C. during this interval. The mixture so produced was rolled and sheeted on a two roll mill at 140° C. to 150° C. The sheet so produced was given six end-passes through the mill bight.

- 25 A 10 inch by 10 inch by .075 inch panel was produced by compression moulding the product produced on the roll mill. The compression moulding was conducted at 170° C. and at 6000 to 8000 psi for 8 minutes.

- 30 A 2 inch square sample of the panel so produced was placed in contact with a moulded sheet of cellulose butyrate-acetate and was kept in intimate contact with the surface thereof by placing a 250 gram weight on the sample. The weighted sample and the cellulose butyrate-acetate were left in contact for 4 35 days at 60° C. No Marring of the cellulose

butyrate-acetate surface was observed at the end of the four days.

EXAMPLE VII.

Six mixtures were prepared. The plastisols contained 100 parts by weight of a vinyl chloride homopolymer, 2 parts by weight dibasic lead phosphite, 1 parts by weight dibasic lead stearate and from 50 to 66 $\frac{2}{3}$ parts by weight of the plasticizers shown below. 40 45

The method of preparing and fusing the mixtures comprised the following steps: The ingredients were mixed in a blender at about room temperature for 10 minutes until a smooth fluid paste was formed. The paste was poured into a mould whose dimensions were 8 in. × 8 in. × 0.020 in. The mould was placed in an open press and heated for about 4 minutes at 170° C. The lid of the mould was put on, the press platens were closed, a pressure of 100 psi was applied to the mould and the mixture was heated for 8 minutes at 170° C. Then the pressure was raised to 4000 psi and the mixture heated for about 7 minutes at 170° C. The product was allowed to cool, removed from the mould and then a sample of the product immersed in ethyl acetate. After immersion, the sample was found to be strong, rubbery and homogeneous in all six compositions prepared, and this treatment demonstrated that a well fused product had been obtained. Poorly fused products tend to disintegrate when immersed in ethyl acetate. Another sample of each of the products was tested and the following results were obtained. 50 55 60 65 70

Plasticizer	Parts of Plasticizer by Weight	Marring (%)
di-2-ethylhexyl phthalate	50	56
di-2-ethylhexyl phthalate	60	80
di-2-ethylhexyl phthalate	66 $\frac{2}{3}$	85
di-2-ethylhexyl isophthalate	50*	14
di-2-ethylhexyl isophthalate	60*	31
di-2-ethylhexyl isophthalate	66 $\frac{2}{3}$	52

*These compositions are useful in producing foam cushions

Following the procedure outlined in this example, a mixture may be prepared containing 100 parts by weight of a vinyl chloride

homopolymer, 2 parts by weight of dibasic lead phosphite, 1 part by weight of dibasic lead stearate and 50 parts by weight of a 75

mixture of plasticizers containing 85% by weight of dioctyl isophthalate and 15% by weight of dioctyl terephthalate. This mixture could be used in the above-described manner to produce a product that would be essentially substantially non-marring.

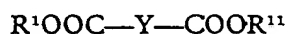
EXAMPLE VIII.

Two mixtures were prepared, one containing 50 parts by weight and the other containing 60 parts by weight of a "mixed" plasticizer. The other components of the mixtures were 100 parts by weight of a vinyl chloride homopolymer, 2 parts by weight of dibasic lead phosphite and 1 part by weight of dibasic lead stearate. The components were mixed and caused to fuse as described in Example VII. The "mixed" plasticizer was prepared by esterifying isophthalic acid with a mixture containing 50% 2-ethylhexyl alcohol and 50% decyl alcohol that had been produced by reacting carbon monoxide, an olefin and hydrogen in the presence of a catalyst such as iron carbonyl.

The fused products obtained had marring values of less than ten per cent. Mixtures such as those used in this example are useful in producing upholstery sheeting.

WHAT WE CLAIM IS:—

1. A resinous mixture having improved non-marring characteristics, which comprises a vinyl chloride resin containing at least 85% by weight of polymerized vinyl chloride, and an organic ester having the formula:



in which Y is a meta- or para-phenylene radical R¹ is an alkyl radical containing 4 to 12 carbon atoms, and R¹¹ is an alkyl radical containing 4 to 12 carbon atoms or a phenyl, alkaryl or an aralkyl radical.

2. A resinous mixture as claimed in claim 1, in which the vinyl chloride has been co-

polymerized with a vinyl ester, vinyl ether, vinyl ketone, vinyl or vinylidene halide, acrylic compound, or allylic compound.

3. A resinous mixture as claimed in either of the preceding claims in which the ester is present in amounts of from 15 to 100 parts by weight per 100 parts by weight of the vinyl chloride resin.

4. A resinous mixture as claimed in claim 3 when made by a hot-processing method which method comprises mechanically compounding the mix comprising the vinyl chloride resin and the ester at a shearing pressure and a temperature high enough to flux the resin.

5. A resinous mixture as claimed in claim 3 in which the ester is present in amount of from 15 to 60 parts by weight per 100 parts by weight of the vinyl chloride resin.

6. A resinous mixture as claimed in claim 5 when made by a cold-processing method which method comprises mechanically compounding the mix comprising the vinyl chloride resin and the ester at about room temperature to give a plastisol.

7. A resinous mixture as claimed in claim 6 in which the vinyl chloride resin has a particle diameter of from 0.05 to 2.0 microns.

8. A resinous mixture as claimed in any one of the preceding claims, in which two or more esters are present therein at least one of the esters being an ester having a formula as given in claim 1.

9. A resinous mixture having improved non-marring characteristics as claimed in claim 1 substantially as described with reference to any one of the specific examples hereinbefore set forth.

10. Articles when produced from or coated with the resinous mixture as claimed in any one of claims 1 to 9.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.

THIS PAGE BLANK (USPTO)